

Bis(3-hydroxypyridinium) fumarate

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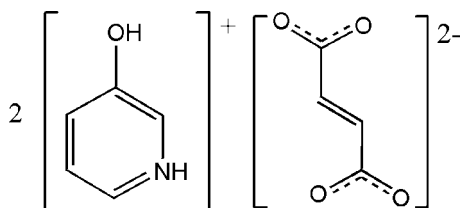
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.100; data-to-parameter ratio = 12.7.

The crystal structure of the title compound, $2\text{C}_5\text{H}_6\text{NO}_2^+ \cdot \text{C}_4\text{H}_2\text{O}_4^{2-}$, consists of 3-hydroxypyridinium cations and fumarate dianions. The dianion is located on an inversion center and the cation is linked to it by $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. The cation is twisted with respect to the anion by 24.83 (5)°.

Related literature

For general background, see: Thomas *et al.* (2007); Fidler *et al.* (2003); Zhang *et al.* (2004). For the ionization of hydroxypyridine in the solution, see: Lezina *et al.* (1981). For 3-hydroxypyridinium salts, see: Aakeroy & Nieuwenhuyzen (1994); Fukunaga *et al.* (2004). For co-crystals of neutral pyridine derivatives and neutral fumaric acid, see: Bowes *et al.* (2003); Aakeroy *et al.* (2002); Haynes *et al.* (2006); Bu *et al.* (2007); Xu *et al.* (2009). For C—O bond distances in the deprotonated carboxyl groups of fumarates, see: Liu *et al.* (2003); Liu & Xu (2004); Xu *et al.* (2009).



Experimental

Crystal data

$2\text{C}_5\text{H}_6\text{NO}^+ \cdot \text{C}_4\text{H}_2\text{O}_4^{2-}$
 $M_r = 306.27$
 Monoclinic, $P2_1/n$
 $a = 3.8037$ (5) Å
 $b = 10.4798$ (13) Å
 $c = 17.423$ (2) Å
 $\beta = 90.360$ (5)°

$V = 694.52$ (15) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 294$ K
 $0.32 \times 0.28 \times 0.24$ mm

Data collection

Rigaku R-AXIS RAPID IP
 diffractometer
 Absorption correction: none
 7561 measured reflections

1359 independent reflections
 1237 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.100$
 $S = 1.07$
 1359 reflections
 107 parameters
 2 restraints

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.14$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O1}$	0.893 (12)	1.687 (12)	2.5774 (14)	175.2 (18)
$\text{O3}-\text{H3A} \cdots \text{O2}^{\dagger}$	0.839 (14)	1.751 (15)	2.5831 (15)	171.5 (16)

Symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2594).

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supplementary materials

Acta Cryst. (2009). E65, o1679 [doi:10.1107/S1600536809023800]

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Comment

The hydroxypyridine derivatives and the fumaric acid have been extensively applied in biological and medicine fields (Zhang *et al.*, 2004; Thomas *et al.*, 2007; Fidler *et al.*, 2003). Although the carboxyl group of the fumaric acid is usually deprotonated while the pyridine derivatives are protonated in the solution (Lezina *et al.*, 1981), some crystal structures showed that they also exist as co-crystal of neutral molecules (Bowes *et al.* 2003; Aakeroy *et al.*, 2002; Haynes *et al.* 2006; Xu *et al.* 2009). Herein we report the crystal structure of the title compound containing pyridine derivative and fumaric acid components.

The crystal structure of the title compound consists of fumarate anions and 3-hydroxypyridinium cations (Fig. 1). The planar fumarate anion is located in an inversion center. The C1—O1 bond distance of 1.2603 (15) Å is similar to C1—O2 bond distance of 1.2452 (15) Å, it agrees with those found in metal complexes of fumarate (Liu *et al.* 2003; Liu & Xu, 2004).

The 3-hydroxypyridine is protonated in the crystal structure, the geometry data is consistent with those in crystal structures of 3-hydroxypyridinium hydrogen *L*-malate (Aakeroy & Nieuwenhuyzen, 1994) and 3-hydroxypyridinium hydrogen tartronate (Fukunaga *et al.* 2004).

In the crystal structure the planar hydroxypyridinium cation is twisted respect to the planar fumarate with a dihedral angle of 24.83 (5)°, and links with the fumarate anions *via* N—H···O and O—H···O hydrogen bonding (Table 1 and Fig. 2).

Experimental

Reagents and solvent were used as purchased without further purification. 3-Hydroxypyridine (2 mmol) and fumaric acid (1 mmol) were dissolved in ethanol (5 ml) at room temperature. The single crystals were obtained from the solution after one week.

Refinement

H atoms bonded to N and O atoms were located in a difference Fourier map and were refined with distance restraints of O—H = 0.82±0.01 and N—H = 0.86±0.01 Å; $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N}, \text{O})$. Other H atoms were placed in calculated positions with C—H = 0.93 Å and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

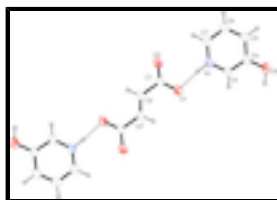


Fig. 1. The molecular structure of the title compound with 40% probability displacement (arbitrary spheres for H atoms). Dashed lines indicate hydrogen bonding [symmetry code: (i) 1 - x, 1 - y, 1 - z].

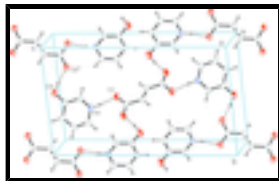
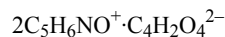


Fig. 2. The unit cell packing diagram showing O—H...O and N—H...O hydrogen bonding (dashed lines) [symmetry code: (ii) $-x + 1/2, y + 1/2, -z + 1/2$].

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Crystal data



$$M_r = 306.27$$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$$a = 3.8037\ (5)\ \text{\AA}$$

$$b = 10.4798\ (13)\ \text{\AA}$$

$$c = 17.423\ (2)\ \text{\AA}$$

$$\beta = 90.360\ (5)^\circ$$

$$V = 694.52\ (15)\ \text{\AA}^3$$

$$Z = 2$$

$$F_{000} = 320$$

$$D_x = 1.465\ \text{Mg m}^{-3}$$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2322 reflections

$$\theta = 2.4\text{--}24.6^\circ$$

$$\mu = 0.12\ \text{mm}^{-1}$$

$$T = 294\ \text{K}$$

Prism, colorless

$$0.32 \times 0.28 \times 0.24\ \text{mm}$$

Data collection

Rigaku R-Axis RAPID IP
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$$T = 294\ \text{K}$$

ω scans

Absorption correction: none

7561 measured reflections

1359 independent reflections

1237 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.024$$

$$\theta_{\text{max}} = 26.0^\circ$$

$$\theta_{\text{min}} = 2.3^\circ$$

$$h = -4 \rightarrow 4$$

$$k = -12 \rightarrow 12$$

$$l = -20 \rightarrow 21$$

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.037$$

$$wR(F^2) = 0.100$$

$$S = 1.07$$

1359 reflections

107 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.1474P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.001$$

$$\Delta\rho_{\text{max}} = 0.25\ \text{e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.14\ \text{e \AA}^{-3}$$

2 restraints

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.116 (10)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.0136 (3)	0.56088 (11)	0.76518 (6)	0.0373 (3)
O1	0.2604 (3)	0.49000 (9)	0.63451 (5)	0.0489 (3)
O2	0.4289 (3)	0.69067 (9)	0.62330 (5)	0.0568 (4)
O3	-0.2084 (3)	0.39098 (10)	0.93748 (6)	0.0559 (3)
C1	0.3982 (3)	0.58033 (12)	0.59760 (7)	0.0368 (3)
C2	0.5267 (3)	0.55371 (13)	0.51822 (7)	0.0375 (3)
H2	0.6522	0.6174	0.4933	0.045*
C3	-0.0215 (3)	0.46506 (12)	0.81483 (7)	0.0357 (3)
H3	0.0526	0.3836	0.8012	0.043*
C4	-0.1676 (3)	0.48541 (12)	0.88672 (7)	0.0366 (3)
C5	-0.2754 (3)	0.60885 (13)	0.90499 (7)	0.0410 (3)
H5	-0.3763	0.6256	0.9524	0.049*
C6	-0.2323 (4)	0.70583 (13)	0.85271 (8)	0.0431 (3)
H6	-0.3019	0.7885	0.8647	0.052*
C7	-0.0849 (4)	0.67954 (13)	0.78221 (8)	0.0418 (3)
H7	-0.0543	0.7447	0.7466	0.050*
H1	0.103 (4)	0.5407 (17)	0.7195 (6)	0.063*
H3A	-0.127 (5)	0.3217 (12)	0.9213 (10)	0.063*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0428 (6)	0.0421 (6)	0.0271 (5)	-0.0016 (5)	0.0072 (4)	0.0009 (4)
O1	0.0743 (7)	0.0392 (6)	0.0333 (5)	-0.0081 (4)	0.0207 (5)	-0.0027 (4)
O2	0.0928 (9)	0.0383 (6)	0.0397 (6)	-0.0108 (5)	0.0225 (5)	-0.0095 (4)
O3	0.0852 (8)	0.0450 (6)	0.0378 (6)	0.0079 (5)	0.0253 (5)	0.0091 (4)
C1	0.0467 (7)	0.0355 (7)	0.0283 (6)	-0.0003 (5)	0.0071 (5)	-0.0027 (5)
C2	0.0468 (7)	0.0369 (7)	0.0290 (6)	-0.0030 (5)	0.0103 (5)	0.0003 (5)
C3	0.0420 (7)	0.0342 (6)	0.0310 (6)	0.0005 (5)	0.0076 (5)	-0.0018 (5)

supplementary materials

C4	0.0407 (7)	0.0406 (7)	0.0285 (6)	-0.0012 (5)	0.0072 (5)	0.0016 (5)
C5	0.0441 (7)	0.0472 (8)	0.0318 (6)	0.0042 (6)	0.0087 (5)	-0.0056 (6)
C6	0.0481 (7)	0.0363 (7)	0.0450 (7)	0.0055 (5)	0.0039 (6)	-0.0043 (5)
C7	0.0482 (8)	0.0386 (7)	0.0387 (7)	-0.0001 (5)	0.0044 (5)	0.0067 (5)

Geometric parameters (Å, °)

N1—C7	1.3327 (17)	C2—H2	0.9300
N1—C3	1.3327 (16)	C3—C4	1.3898 (17)
N1—H1	0.893 (12)	C3—H3	0.9300
O1—C1	1.2603 (15)	C4—C5	1.3945 (18)
O2—C1	1.2452 (15)	C5—C6	1.3752 (19)
O3—C4	1.3369 (15)	C5—H5	0.9300
O3—H3A	0.839 (14)	C6—C7	1.3813 (19)
C1—C2	1.4962 (16)	C6—H6	0.9300
C2—C2 ⁱ	1.308 (3)	C7—H7	0.9300
C7—N1—C3	121.94 (11)	O3—C4—C3	122.09 (12)
C7—N1—H1	121.9 (12)	O3—C4—C5	120.01 (11)
C3—N1—H1	116.2 (12)	C3—C4—C5	117.90 (11)
C4—O3—H3A	111.9 (13)	C6—C5—C4	119.86 (11)
O2—C1—O1	123.54 (11)	C6—C5—H5	120.1
O2—C1—C2	118.36 (11)	C4—C5—H5	120.1
O1—C1—C2	118.10 (11)	C5—C6—C7	119.49 (12)
C2 ⁱ —C2—C1	123.96 (15)	C5—C6—H6	120.3
C2 ⁱ —C2—H2	118.0	C7—C6—H6	120.3
C1—C2—H2	118.0	N1—C7—C6	120.03 (12)
N1—C3—C4	120.77 (12)	N1—C7—H7	120.0
N1—C3—H3	119.6	C6—C7—H7	120.0
C4—C3—H3	119.6		

Symmetry codes: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O1	0.893 (12)	1.687 (12)	2.5774 (14)	175.2 (18)
O3—H3A \cdots O2 ⁱⁱ	0.839 (14)	1.751 (15)	2.5831 (15)	171.5 (16)

Symmetry codes: (ii) $-x+1/2, y-1/2, -z+3/2$.

Fig. 1

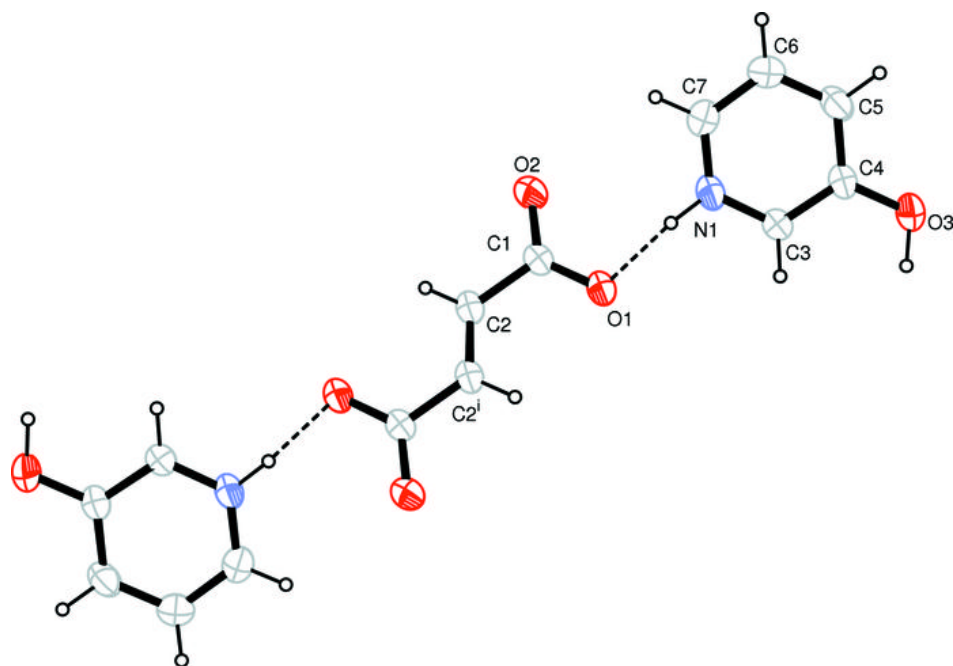


Fig. 2

